

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
13 January 2005 (13.01.2005)

PCT

(10) International Publication Number
WO 2005/003053 A1

(51) International Patent Classification⁷: C04B 28/02,
24/26, 24/38, 26/28, 22/12, E21B 33/13

C04B 28/02,

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(21) International Application Number:
PCT/GB2004/001648

(22) International Filing Date: 15 April 2004 (15.04.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/608,748 27 June 2003 (27.06.2003) US

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2005/003053 A1

(54) Title: CEMENT COMPOSITIONS WITH IMPROVED FLUID LOSS CHARACTERISTICS AND METHODS OF CEMENTING IN SURFACE AND SUBTERRANEAN APPLICATIONS

(57) Abstract: The present invention provides cement compositions comprising an improved fluid loss control additive, and methods for cementing using such cement compositions. Exemplary embodiments of the cement compositions comprise a hydraulic cement, water, and a fluid loss control additive comprising an acrylamide copolymer derivative, a dispersant, and a hydratable polymer. Optionally, other additives suitable for inclusion in cement compositions may be added.

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CEMENT COMPOSITIONS WITH IMPROVED FLUID LOSS CHARACTERISTICS AND METHODS OF CEMENTING IN SURFACE AND SUBTERRANEAN APPLICATIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to cementing operations, and more particularly, to cement compositions comprising an improved fluid loss control additive, and methods of using such compositions in surface and subterranean applications.

2. Description of the Prior Art

Hydraulic cement compositions are commonly utilized in subterranean operations, particularly subterranean well completion and remedial operations. For example, hydraulic cement compositions are used in primary cementing operations whereby pipe strings such as casings and liners are cemented in well bores. In performing primary cementing, hydraulic cement compositions are pumped into the annular space between the walls of a well bore and the exterior surface of the pipe string disposed therein. The cement composition is permitted to set in the annular space, thereby forming an annular sheath of hardened substantially impermeable cement therein that substantially supports and positions the pipe string in the well bore and bonds the exterior surface of the pipe string to the walls of the well bore. Hydraulic cement compositions also are used in remedial cementing operations such as plugging highly permeable zones or fractures in well bores, plugging cracks and holes in pipe strings, and the like.

In order for such well cementing operations to be successful, the cement compositions utilized must include a fluid loss control additive to reduce the loss of fluid, e.g., water, from the cement compositions when they contact permeable subterranean formations and zones. Excessive fluid loss, *inter alia*, causes a cement composition to be prematurely dehydrated, which limits the amount of cement composition that can be pumped, decreases the compressive strength of the cement composition, and prevents or reduces bond strength between the set cement composition and the subterranean zone, the walls of pipe, and/or the walls of the well bore. Fluid loss control agents may also be used in surface cement compositions.

Conventional contemporary synthetic fluid loss control additives are large, water-soluble polymers that are capable of functioning at a wider range of temperatures. An

example of such synthetic fluid loss control additive is a fluid loss additive consisting of hydrolyzed copolymers of acrylamide ("AA") and 2-acrylamido, 2-methyl propane sulfonic acid ("AMPS"). However, certain of these AA/AMPS copolymers are useful only in operations where the bottom hole circulating temperature ("BHCT") ranges from about 90°F to about 125°F, whereas BHCT ranges encountered in such operations are often outside such a range. Still further, certain of these copolymers have a salt tolerance of only up to about 10%.

The temperature limitations of certain of the AA/AMPS copolymers, *e.g.*, ineffectiveness at temperatures above about 125°F BHCT, are believed to be the result of hydrolysis of the amide groups. The carboxylate groups formed by such hydrolysis convert the copolymers to materials which function to retard the setting of the cement and to reduce the compressive strength of the set cement. Further, in the lower portion of the above-mentioned temperature range (between about 90°F to about 100°F) certain of the AA/AMPS copolymers are less effective as a fluid loss additive, requiring inclusion of larger amounts of such additive than at higher temperatures. The inclusion of a sufficiently large amount of a fluid loss control additive to create a cement composition with acceptable fluid loss often creates viscosity and pumpability problems, since the addition of such copolymer directly affects the resultant slurry rheology. Certain copolymers of acrylamide and AMPS exhibit high viscosity and poor mixability, resulting in cement slurries having poor pumpability characteristics during cementing operations. Mixability is a subjective term used to describe how well the components in the cement composition wet and mix with each other, as well as the energy required to create a generally homogeneous slurry.

SUMMARY OF THE INVENTION

The present invention relates to cementing operations, and more particularly, to cement compositions comprising an improved fluid loss control additive, and methods of using such compositions in surface and subterranean applications.

One method of the present invention comprises the steps of providing a cement composition comprising a hydraulic cement, water, and a fluid loss control additive comprising an acrylamide copolymer derivative, a dispersant, and a hydratable polymer; placing the cement composition into the subterranean formation; and permitting the cement composition to set therein.

One exemplary embodiment of the cement compositions of the present invention comprises a hydraulic cement, water, and a fluid loss control additive comprising an acrylamide copolymer derivative, a dispersant and a hydratable polymer. Optionally, other additives suitable for inclusion in cement compositions may be added.

The objects, features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the preferred embodiments, which follows.

DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention relates to cementing operations, and more particularly, to cement compositions comprising an improved fluid loss control additive, and methods of using such compositions in surface and subterranean applications. While the compositions and methods of the present invention are useful in a variety of applications, they are particularly useful for subterranean well completion and remedial operations, such as primary cementing, *e.g.*, cementing casings and liners in well bores, including those in production wells, which include multi-lateral subterranean wells. They are also useful for surface cementing operations, including construction cementing operations.

The cement compositions of the present invention generally comprise a cement, water sufficient to form a pumpable slurry, and a fluid loss control additive of the present invention. A wide variety of optional additives may be included in the cement compositions of the present invention if desired. The cement compositions of the present invention may range in density from about 5 lb/gallon to about 30 lb/gallon. In one embodiment, the cement compositions of the present invention range in density from about 8 lb/gallon to about 20 lb/gallon.

Any cements suitable for use in subterranean applications are suitable for use in the present invention. Furthermore, any cements suitable for use in surface applications, *e.g.*, construction cements, are suitable for use in the present invention. In one embodiment, the improved cement compositions of the present invention comprise a hydraulic cement. A variety of hydraulic cements are suitable for use including those comprised of calcium, aluminum, silicon, oxygen, and/or sulfur, which set and harden by reaction with water. Such hydraulic cements include, but are not limited to, Portland cements, pozzolana cements, gypsum cements, high alumina content cements, silica cements, and high alkalinity cements.

The water present in the cement compositions of the present invention may be from any source provided that it does not contain an excess of compounds that adversely affect other compounds in the cement compositions. For example, a cement composition of the present invention can comprise fresh water, salt water (e.g., water containing one or more salts dissolved therein), brine (e.g., saturated salt water), or seawater. The water may be present in an amount sufficient to form a pumpable slurry. Generally, the water is present in the cement compositions of the present invention in an amount in the range of from about 15% to about 200% by weight of cement ("bwoc") therein. In certain embodiments, the water is present in the cement compositions of the present invention in an amount in the range of from about 25% to about 60% bwoc therein.

The improved fluid loss control additives of the present invention generally comprise an acrylamide copolymer derivative, a hydratable polymer, and a dispersant. Certain embodiments comprise an acrylamide copolymer derivative and a hydratable polymer. Certain other embodiments comprise an acrylamide copolymer derivative and a dispersant. Optionally, other additives may be added, such as, for example, a zeolite, iron chloride, an organic acid, and the like.

The fluid loss additives of the present invention comprise an acrylamide copolymer derivative. As referred to herein, the term "copolymer" will be understood to mean a polymer comprising a plurality of compounds. For example, a "copolymer" may comprise, *inter alia*, a graft polymer wherein one monomer is grafted onto a backbone comprising another monomer. Any compound comprising 2-acrylamido-2-methylpropane sulfonic acid, or acid salts thereof, will be an "acrylamide copolymer derivative" as that term is used herein. An example of a suitable acrylamide copolymer derivative comprises a copolymer, or copolymer salt, of N,N-dimethylacrylamide and 2-acrylamido-2-methylpropane sulfonic acid, or acid salts thereof. Another example of a suitable acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member selected from the group consisting of lignin, lignite and their salts, and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals. Another example of a suitable acrylamide copolymer derivative comprises a graft polymer comprising a backbone

comprising at least one member selected from the group consisting of derivatized cellulose, polyvinyl alcohol, polyethylene oxide, polypropylene oxide, and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals. Such examples of suitable acrylamide copolymer derivatives are described in U.S. Pat. Nos. 4,015,991; 4,515,635; 4,555,269; 4,676,317; 4,703,801; and 6,268,406, the relevant disclosures of which are incorporated herein by reference. An additional example of a suitable acrylamide copolymer derivative comprises copolymers or copolymer salts comprising 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof; for example, wherein the copolymers or copolymer salts comprise copolymers of hydrolyzed acrylamide and 2-acrylamido-2-methylpropane sulfonic acid derivatives. Examples of suitable commercially available acrylamide copolymer derivatives include, *inter alia*, those commercially available from Halliburton Energy Services, Inc., of Duncan, Oklahoma, under the tradenames "HALAD®-344"; "HALAD®-413"; "HALAD®-4" and "HALAD®-700". In certain embodiments where the acrylamide copolymer derivative comprises a copolymer or copolymer salt of N,N-dimethylacrylamide and 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof, the copolymer, or copolymer salt, may have a N,N-dimethylacrylamide to 2-acrylamido-2-methylpropane sulfonic acid (or acid salts thereof) mole ratio of from about 1:4 to about 4:1. In certain embodiments, the copolymer, or copolymer salt, may have a weight average molecular weight of between about 75,000 and about 300,000 daltons. Generally, the acrylamide copolymer derivative is present in the fluid loss control additives of the present invention in an amount in the range of from about 1% to about 99% by weight. In one embodiment, the acrylamide copolymer derivative is present in the fluid loss control additive in an amount in the range of from about 30% to about 60% by weight.

Certain embodiments of the fluid loss control additive of the present invention comprise a dispersant. Where present, the dispersant in the fluid loss control additive acts, *inter alia*, to control the rheology of the cement composition and to stabilize the cement composition over a broad density range. While a variety of dispersants known to those skilled in the art may be used in accordance with the present invention, a preferred dispersant is a water-soluble polymer prepared by the caustic-catalyzed condensation of formaldehyde

with acetone wherein the polymer contains sodium sulfate groups. Such a preferred dispersant is commercially available under the trade designation "CFR-3TM" from Halliburton Energy Services, Inc., of Duncan, Oklahoma. Another suitable dispersant is commercially available under the trade designation "CFR-2TM," also from Halliburton Energy Services, Inc., of Duncan, Oklahoma. Another source of a suitable dispersant is a multi-purpose cement additive commercially available under the trade designation "UNIVERSAL CEMENT SYSTEMSTM" from Halliburton Energy Services, Inc., of Duncan, Oklahoma; such additive is disclosed in U.S. Patent Nos. 5,749,418; 5,968,255; and 5,972,103, the relevant disclosures of which are herein incorporated by reference. Generally, the dispersant is present in the fluid loss control additive in an amount sufficient to prevent gelation of the cement composition. In some embodiments, the dispersant is present in the fluid loss control additive in an amount in the range of from about 25% to about 50% by weight. In one embodiment, the dispersant is present in the fluid loss control additive in an amount in the range of from about 30% to about 40% by weight.

Certain embodiments of the present invention comprise a hydratable polymer. Where present, the hydratable polymer in the fluid loss control additive acts, *inter alia*, to increase the viscosity of the cement composition in which the fluid loss control additive is used. Various hydratable polymers can be utilized in the fluid loss control additive including, but not limited to, carboxymethylcellulose, hydroxyethylcellulose, carboxymethylhydroxyethylcellulose, vinyl sulfonated polymers, and hydratable graft polymers. An example of a suitable hydratable polymer is a cellulose derivative commercially available from Dow Chemical Co., under the tradename "CARBOTRON 20." Another source of a suitable hydratable polymer is a multi-purpose cement additive commercially available under the trade designation "UNIVERSAL CEMENT SYSTEMSTM" from Halliburton Energy Services, Inc., of Duncan, Oklahoma; such additive is disclosed in U.S. Patent Nos. 5,749,418; 5,968,255; and 5,972,103, the relevant disclosures of which are herein incorporated by reference. Where utilized, the hydratable polymer is present in the fluid loss control additive in an amount sufficient to contribute a desired degree of viscosity to the cement composition. Generally, the hydratable polymer is present in the fluid loss control additive in an amount in the range of from about 0.1% to about 15% by weight. In one embodiment, the hydratable polymer is present in the fluid loss control additive in an amount in the range of from about 1.0% to about 5% by weight.

Optionally, the fluid loss control additives of the present invention may comprise a zeolite. Where used, the zeolite functions, *inter alia*, to improve the suspension of the fluid loss control additive in a cement slurry. The zeolite further comprises a mixture of chabazite and amorphous silica. The chabazite is present in the zeolite in an amount in the range of from about 50% by weight to about 75% by weight. In certain preferred embodiments, the chabazite is present in the zeolite in an amount in the range of from about 65% by weight to about 70% by weight. The amorphous silica is generally present in the zeolite in an amount in the range of from about 25% by weight to about 50% by weight. In certain preferred embodiments, the amorphous silica is present in the zeolite in an amount in the range of from about 30% by weight to about 35% by weight. An example of a suitable source of zeolite is available from the C2C Zeolite Corporation of Calgary, Canada. Where used, the zeolite is generally present in the fluid loss control additive in an amount in the range of from about 0.1% by weight to about 15% by weight. In certain embodiments, the zeolite is present in the fluid loss control additive in an amount in the range of from about 3% by weight to about 7% by weight.

Optionally, in certain embodiments, the fluid loss control additives of the present invention may comprise iron chloride. Where used, the iron chloride may be ferrous chloride, ferric chloride, or mixtures thereof. The iron chloride functions, *inter alia*, in combination with other components which may be present, to aid the cement composition in hydrating in a predictable manner. *Inter alia*, the iron chloride component may also improve the compressive strength of the cement composition in which it is used. In one embodiment, the iron chloride used in the improved fluid loss control additives of the present invention is anhydrous ferric chloride. An example of a suitable source of anhydrous ferric chloride is commercially available from BASF Corporation in Germany. Where used, the iron chloride is present in the fluid loss control additive in an amount sufficient to allow the cement to be suitable for the subterranean environment of the well being cemented. More particularly, the iron chloride may be present in the fluid loss control additive in an amount in the range of from about 5% to about 25% by weight. In certain embodiments, the iron chloride may be present in the fluid loss control additive in an amount in the range of from about 10% to about 15% by weight.

In some embodiments, the fluid loss control additive may optionally comprise an organic acid. Where present, the organic acid acts, *inter alia*, to maintain the viscosity of the

cement composition in which the fluid loss control additive is used over a broad density range by helping to prevent gelation of the cement composition. Various organic acids can be utilized in the fluid loss control additive including, but not limited to, tartaric acid, citric acid, gluconic acid, oleic acid, phosphoric acid, and uric acid. An example of a suitable organic acid is commercially available from Halliburton Energy Services, Inc., of Duncan, Oklahoma, under the tradename "HR[®]-25." Other examples of suitable organic acids include, for example, organic acids which have either minimal or no effect on retarding or accelerating the setting of the cement. One of ordinary skill in the art with the benefit of this disclosure will recognize the types of organic acids which are appropriate for inclusion in the improved fluid loss control additives of the present invention. Where used, the organic acid is present in the fluid loss control additive in an amount sufficient to provide a desired degree of viscosity control. Generally, the organic acid is present in the fluid loss control additive in an amount in the range of from about 0.01% to about 5% by weight. In one embodiment, the organic acid is present in the fluid loss control additive in an amount in the range of from about 0.5% to about 2% by weight.

Optionally, the fluid loss control additive may contain a deaggregation agent. Where used, the deaggregation agent functions, *inter alia*, to improve the ability of the fluid loss control additive to flow freely as a powder. The deaggregation agent may also contribute a minor source of silica to the multi-purpose cement additive. An example of a suitable deaggregation agent is commercially available from National Pigment and Chemical Co. under the tradename Mica/Brite X150. Alternatively, quartz or ground sand may be used, though the spherical nature of Mica/Brite X150 particles is thought to contribute to improved flow characteristics for the cement composition. Generally, the deaggregation agent is present in the fluid loss control additive in an amount sufficient to enable the fluid loss control additive to flow freely as a powder. In some embodiments, the deaggregation agent is present in the fluid loss control additive in an amount in the range of from about 1% to about 15% by weight. In one embodiment, the deaggregation agent is present in the fluid loss control additive in an amount in the range of from about 5% to about 10% by weight.

Optionally, the fluid loss control additive may comprise a source of silica. Where present in the fluid loss control additive, the silica assists in maintaining the compressive strength of the cement composition after setting. An example of a suitable source of high surface area amorphous silica is commercially available from Halliburton Energy Services,

Inc., of Duncan, Oklahoma, under the tradename "SILICALITE." Where used, the high surface area amorphous silica is present in the fluid loss control additive in an amount sufficient to provide a desired after-set compressive strength. More particularly, the high surface area amorphous silica is present in the fluid loss control additive in an amount in the range of from about 0.1% to about 15% by weight. In one embodiment, the high surface area amorphous silica is present in the fluid loss control additive in an amount in the range of from about 1% to about 5% by weight.

The improved fluid loss control additives of the present invention may be prepared in a variety of forms, including, *inter alia*, particulates, solutions, suspensions. Generally, the fluid loss control additives of the present invention are present in the cement compositions of the present invention in an amount sufficient to provide a desired level of fluid loss control. More particularly, the fluid loss control additive may be present in the cement composition in an amount in the range of from about 0.01% to about 10% bwoc. In certain preferred embodiments, the fluid loss control additive is present in the cement composition in an amount in the range of from about 0.25% to about 1.5% bwoc.

As will be recognized by those skilled in the art, the cement compositions of this invention also can include additional suitable additives, including, *inter alia*, accelerants, set retarders, defoamers, microspheres, fiber, weighting materials, salts, vitrified shale, fly ash and the like. Any suitable additive may be incorporated within the cement compositions of the present invention. One of ordinary skill in the art with the benefit of this disclosure will be able to recognize where a particular additive is suitable for a particular application.

An exemplary embodiment of a cement composition of the present invention comprises Class H Portland cement, 45% water bwoc, and 0.7% fluid loss control additive of the present invention bwoc. An exemplary embodiment of a fluid loss control additive of the present invention comprises 63.1% acrylamide copolymer derivative, and 36.9% dispersant. Another exemplary embodiment of a fluid loss control additive of the present invention comprises 95.7% acrylamide copolymer derivative, and 4.3% hydratable polymer.

A method of the present invention comprises providing a cement composition that comprises a cement, water sufficient to form a pumpable slurry, and a fluid loss control additive of the present invention; placing this cement composition in a subterranean formation; and permitting the cement composition to set therein.

To facilitate a better understanding of the present invention, the following illustrative examples of some of the preferred exemplary embodiments are given. In no way should such examples be read to limit the scope of the invention.

EXAMPLE 1

Sample compositions were prepared by mixing a cement slurry with a fluid loss additive according to the following procedure. Each sample was dry blended, then mixed for 35 seconds at 13,000 rpm in a blender. Next, the sample was conditioned for 20 minutes at 125°F in an atmospheric consistometer. After the sample was poured into a preheated cell with a 325 mesh screen, a fluid loss test was performed for 30 minutes at 1,000 psi and 125°F, in accordance with API RP 10B, Recommended Practices for Testing Well Cements.

Sample Composition No. 1 comprises a 15.6 lb/gallon ("ppg") slurry of Texas Lehigh Class A cement, with no fluid loss additives. The fluid loss was found to be 1,574 cubic centimeters.

Sample Composition No. 2 was prepared by mixing 0.5% of Universal Cement Systems™ multi-purpose cement additive by weight of cement with a 15.6 ppg slurry of Texas Lehigh Class A cement. The fluid loss was found to be 1,175 cubic centimeters.

Sample Composition No. 3 was prepared by mixing 0.35% of an acrylamide copolymer derivative (HALAD®-344) by weight of cement with a 15.8 ppg slurry of an experimental cement bearing compositional similarities to a Class H cement. The fluid loss was found to be 270 cubic centimeters.

Sample Composition No. 4 was prepared by mixing 0.7% of a fluid loss control additive with a 15.8 ppg slurry of an experimental cement bearing compositional similarities to a Class H cement. The fluid loss control additive comprised a 1:1 mixture of an acrylamide copolymer derivative (HALAD®-344) and Universal Cement Systems™ multi-purpose cement additive. Accordingly, Sample Composition No. 4 contained 0.35% HALAD®-344 by weight of cement and 0.35% Universal Cement Systems™ multi-purpose cement additive by weight of cement. The fluid loss was found to be 112 cubic centimeters.

Sample Composition No. 5 was prepared by mixing 0.5% of an acrylamide copolymer derivative (HALAD®-344) by weight of cement with a 15.8 ppg slurry of an experimental cement bearing compositional similarities to a Class H cement. The fluid loss was found to be 80 cubic centimeters.

A summary of the fluid loss demonstrated by each of the samples is depicted in Table 1, below.

TABLE 1

FLUID	% Universal Cement Systems™	% HALAD®-344	FLUID LOSS (cc)
Sample Composition No. 1	0	0	1,574
Sample Composition No. 2	0.5	0	1,175
Sample Composition No. 3	0	0.35	270
Sample Composition No. 4	0.35	0.35	112
Sample Composition No. 5	0	0.5	80

Thus, Example 1 demonstrates, *inter alia*, that the use of a fluid loss control additive comprising a reduced dose of an acrylamide copolymer derivative delivers performance comparable to a larger dose of an acrylamide copolymer derivative.

EXAMPLE 2

Sample Composition No. 4 was then permitted to age for a period of two days, and a period of ten days. After each time period had elapsed, a fluid loss test was again performed for 30 minutes at 1,000 psi and 125°F. After aging for a total of two days, Sample Composition No. 4 demonstrated a fluid loss of 84 cubic centimeters. After aging for a total of ten days, Sample Composition No. 4 demonstrated a fluid loss of 76 cubic centimeters. This Example demonstrates, *inter alia*, that the use of a fluid loss control additive comprising a reduced dose of acrylamide copolymer derivative, can deliver performance equal to or superior to a larger dose of acrylamide copolymer derivative.

EXAMPLE 3

Sample compositions were prepared by mixing a cement slurry with a fluid loss additive according to the following procedure. Each sample was dry blended, then mixed for

35 seconds at 13,000 rpm in a blender. Next, the sample was conditioned for 20 minutes at 125°F in an atmospheric consistometer. After the sample was poured into a preheated cell with a 325 mesh screen, a fluid loss test was performed for 30 minutes at 1,000 psi and 125°F, in accordance with API RP 10B, Recommended Practices for Testing Well Cements.

Sample Composition No. 6 was prepared by mixing 0.5% of an acrylamide copolymer derivative (HALAD®-413) by weight of cement with a 15.8 ppg slurry of an experimental cement bearing compositional similarities to a Class H cement. The fluid loss was found to be 615 cubic centimeters.

Sample Composition No. 7 was prepared by mixing a 15.8 ppg slurry of an experimental cement bearing compositional similarities to a Class H cement with 1.0% of a fluid loss additive comprising a 1:1 mixture of Universal Cement Systems™ multi-purpose cement additive with an acrylamide copolymer derivative (HALAD®-413); accordingly, Sample Composition No. 7 contained 0.5% HALAD®-413 by weight of cement and 0.5% Universal Cement Systems™ multi-purpose cement additive by weight of cement. The fluid loss was found to be 212 cubic centimeters.

Sample Composition No. 8 was prepared by mixing 0.7% of an acrylamide copolymer derivative (HALAD®-413) by weight of cement with a 15.8 ppg slurry of an experimental cement bearing compositional similarities to a Class H cement. The fluid loss was found to be 188 cubic centimeters.

Sample Composition No. 9 was prepared by mixing 0.5% of an acrylamide copolymer derivative (HALAD®-4) by weight of cement with a 15.8 ppg slurry of an experimental cement bearing compositional similarities to a Class H cement. The fluid loss was found to be 196 cubic centimeters.

Sample Composition No. 10 was prepared by mixing a 15.8 ppg slurry of an experimental cement bearing compositional similarities to a Class H cement with 1.0% of a fluid loss control additive comprising a 1:1 mixture of Universal Cement Systems™ multi-purpose cement additive and an acrylamide copolymer derivative (HALAD®-4); accordingly, Sample Composition No. 10 contained 0.5% HALAD®-4 by weight of cement and 0.5% Universal Cement Systems™ multi-purpose cement additive by weight of cement. The fluid loss was found to be 100 cubic centimeters.

Sample Composition No. 11 was prepared by mixing 0.7% of an acrylamide copolymer derivative (HALAD®-4) by weight of cement with a 15.8 ppg slurry of an

experimental cement bearing compositional similarities to a Class H cement. The fluid loss was found to be 64 cubic centimeters.

A summary of the fluid loss demonstrated by each of the samples is depicted in Table 2, below.

TABLE 2

FLUID	% Universal Cement Systems™	% HALAD®-413	% HALAD®-4	FLUID LOSS (cc)
Sample Composition No. 6	0	0.5	0	615
Sample Composition No. 7	0.5	0.5	0	212
Sample Composition No. 8	0	0.7	0	188
Sample Composition No. 9	0	0	0.5	196
Sample Composition No. 10	0.5	0	0.5	100
Sample Composition No. 11	0	0	0.7	64

Universal Cement Systems™ multi-purpose cement additive comprises a hydratable polymer and a dispersant. Example 3 demonstrates, *inter alia*, that the use of an improved fluid loss control additive comprising a hydratable polymer, a dispersant, and a reduced dose of an acrylamide copolymer derivative provides comparable fluid loss control to a fluid loss control additive comprising a larger dose of an acrylamide copolymer derivative. *Inter alia*, Example 3 also demonstrates that a variety of acrylamide copolymer derivatives are suitable for combination with, *inter alia*, a hydratable polymer and a dispersant, in the fluid loss control additives of the present invention.

EXAMPLE 4

Sample compositions were prepared by mixing a cement slurry with a fluid loss additive according to the following procedure. Each sample was dry blended, then mixed for

35 seconds at 13,000 rpm in a blender. Next, the sample was conditioned for 20 minutes at 190°F in an atmospheric consistometer. After the sample was poured into a preheated cell with a 325 mesh screen, a fluid loss test was performed per API Specification 10.7 for 30 minutes at 1,000 psi and 205°F.

Sample Composition No. 12 was prepared by mixing 0.49% of an acrylamide copolymer derivative (HALAD®-344) by weight of cement with a 15.8 ppg slurry of an experimental cement bearing compositional similarities to a Class H cement. The fluid loss at 1,000 psi and 205°F was found to be 220 cubic centimeters.

Sample Composition No. 13 was prepared by mixing 0.98% of a fluid loss control additive of the present invention with a 15.8 ppg slurry of an experimental cement bearing compositional similarities to a Class H cement. The fluid loss control additive comprised a 1:1 mixture of Universal Cement Systems™ multi-purpose cement additive and an acrylamide copolymer derivative (HALAD®-344); accordingly, Sample Composition No. 13 contained 0.49% HALAD®-344 by weight of cement and 0.49% Universal Cement Systems™ multi-purpose cement additive by weight of cement. The fluid loss at 1,000 psi and 205°F was found to be 60 cubic centimeters.

Sample Composition No. 14 was prepared by mixing 0.7% of an acrylamide copolymer derivative (HALAD®-344) by weight of cement with a 15.8 ppg slurry of an experimental cement bearing compositional similarities to a Class H cement. The fluid loss at 1,000 psi and 205°F was found to be 44 cubic centimeters.

A summary of the fluid loss demonstrated by each of the samples is depicted in Table 3, below.

TABLE 3

FLUID	% Universal Cement Systems™	% HALAD®-344	FLUID LOSS (cc)
Sample Composition No. 12	0	0.49	220
Sample Composition No. 13	0.49	0.49	60
Sample Composition No. 14	0	0.7	44

Thus, Example 4 demonstrates, *inter alia*, that the use of a fluid loss control additive comprising a reduced dose of an acrylamide copolymer derivative delivers performance comparable to a larger dose of an acrylamide copolymer derivative. Additionally, Example 4 demonstrates that such fluid loss control additive is an effective fluid loss control additive at elevated temperatures and pressures.

EXAMPLE 5

A sample composition was prepared by mixing a cement slurry with a fluid loss additive according to the following procedure. The sample was dry blended, then mixed for 35 seconds at 13,000 rpm in a blender. Next, the sample was conditioned for 60 minutes at 400°F in a stirring fluid loss cell. After the sample was poured into a preheated cell with a 325 mesh screen, a fluid loss test was performed for 30 minutes at 1,000 psi and 400°F.

Sample Composition No. 15 was prepared by mixing 0.84% of a fluid loss control additive of the present invention with a 15.6 ppg slurry comprising 30% "SSA-1" bwoc, and the balance comprising an experimental cement bearing compositional similarities to a Class H cement. SSA-1 is a silica flour additive available from Halliburton Energy Services, Inc., of Houston, Texas. The fluid loss control additive comprised a 1:1 mixture of Universal Cement Systems™ multi-purpose cement additive and an acrylamide copolymer derivative (HALAD®-344); accordingly, Sample Composition No. 15 contained 0.42% HALAD®-344 by weight of cement and 0.42% Universal Cement Systems™ multi-purpose cement additive by weight of cement. The fluid loss at 1,000 psi and 405°F was found to be 400 cubic centimeters.

Inter alia, Example 5 demonstrates that the fluid loss control additive of the present invention provides fluid loss control at elevated temperatures.

EXAMPLE 6

The transition time of a cement composition may be defined as the time period starting when the cement composition has sufficient gel strength to support itself yet cannot prevent influx of formation fluids, and ending when the cement composition achieves sufficient gel strength to prevent the influx of such formation fluids. Experimentally, the transition time may be approximated by measuring the time period in which the gel strength of a cement composition progresses from about 100 lb per 100 ft² to about 500 lb per 100 ft².

The zero-gel time, which may also be referred to as the delayed-gel time, refers to the time period starting when the cement composition is placed in a subterranean formation and ending when the gel strength of the cement composition progresses to about 100 lb per 100 ft², i.e., ending when the cement composition begins its transition time.

Sample compositions were prepared by mixing a cement slurry with a fluid loss additive according to the following procedure. Each sample was dry blended, then mixed for 35 seconds at 13,000 rpm in a blender. Next, the sample was conditioned for 40 minutes to 125°F in a MiniMac® at 5,000 psi. Then, a static gel strength test was performed.

Sample Composition No. 16 was prepared by mixing 0.7% of an acrylamide copolymer derivative (HALAD®-344) by weight of cement with a 15.8 ppg slurry of an experimental cement bearing compositional similarities to a Class H cement. Sample Composition No. 16 demonstrated a zero gel time of 41 minutes, and a transition time of 17 minutes.

Sample Composition No. 17 was prepared by mixing 1.0% of a fluid loss control additive of the present invention with a 15.8 ppg slurry of an experimental cement bearing compositional similarities to a Class H cement. The fluid loss control additive comprised a 1:1 mixture of Universal Cement Systems™ multi-purpose cement additive and an acrylamide copolymer derivative (HALAD®-344); accordingly, Sample Composition No. 17 contained 0.5% HALAD®-344 by weight of cement and 0.5% Universal Cement Systems™ multi-purpose cement additive by weight of cement. Sample Composition No. 17 demonstrated a zero gel time of 1 hour 16 minutes and a transition time of 17 minutes.

A summary of the data from each of the samples is depicted in Table 4, below.

TABLE 4

FLUID	% Universal Cement Systems™	% HALAD®-344	Zero Gel Time (hours: minutes)	Transition Time (minutes)
Sample Composition No. 16	0	0.7	0:41	17
Sample Composition No. 17	0.5	0.5	1:16	17

Thus, Example 6 demonstrates, *inter alia*, that the use of a fluid loss control additive comprising a reduced dose of an acrylamide copolymer derivative delivers performance comparable to a larger dose of the acrylamide copolymer derivative.

EXAMPLE 7

Sample compositions were prepared by mixing a cement slurry with a fluid loss additive according to the following procedure. Each sample was dry blended, then mixed for 35 seconds at 13,000 rpm in a blender. Next, the sample was conditioned for 20 minutes at 125°F in an atmospheric consistometer. After the sample was poured into a preheated cell with a 325 mesh screen, a fluid loss test was performed for 30 minutes at 1,000 psi and 125°F, in accordance with API RP 10B, Recommended Practices for Testing Well Cements.

Sample Composition No. 18 was prepared by mixing 0.7% of a fluid loss additive by weight of cement with a 15.8 ppg slurry of an experimental cement bearing compositional similarities to a Class H cement. The fluid loss additive comprised a 1:1 mixture of Universal Cement Systems™ multi-purpose cement additive with an acrylamide copolymer derivative (HALAD®-344); accordingly, Sample Composition No. 18 contained 0.35% HALAD®-344 by weight of cement and 0.35% Universal Cement Systems™ multi-purpose cement additive by weight of cement. The fluid loss was found to be 80 cubic centimeters.

Sample Composition No. 19 was prepared by mixing a 15.8 ppg slurry of an experimental cement bearing compositional similarities to a Class H cement with 0.7% of a fluid loss additive comprising 47.5% of an acrylamide copolymer derivative (HALAD®-344) by weight, 47.5% Universal Cement Systems™ multi-purpose cement additive by weight, and 5% zeolite by weight. Accordingly, Sample Composition No. 19 contained 0.3325% HALAD®-344 by weight of cement, 0.3325% Universal Cement Systems™ multi-purpose cement additive by weight of cement, and 0.035% zeolite by weight of cement. The fluid loss was found to be 96 cubic centimeters.

Thus, Example 7 demonstrates, *inter alia*, that the use of a fluid loss control additive of the present invention provides acceptable fluid loss control.

EXAMPLE 8

Sample compositions were prepared by mixing a cement slurry with a fluid loss additive according to the following procedure. Each sample was dry blended, then mixed for 35 seconds at 13,000 rpm in a blender. Next, the sample was conditioned for 20 minutes at 125°F in an atmospheric consistometer. After the sample was poured into a preheated cell with a 325 mesh screen, a fluid loss test was performed for 30 minutes at 1,000 psi and 125°F, in accordance with API RP 10B, Recommended Practices for Testing Well Cements.

Sample Composition No. 20 comprises a 15.8 ppg slurry of TXI Class H cement, with no fluid loss control additives. The fluid loss was found to be 1,529 cubic centimeters.

Sample Composition No. 21 was prepared by mixing 0.35% of Universal Cement Systems™ multi-purpose cement additive by weight of cement with a 15.8 ppg slurry of TXI Class H cement. The fluid loss was found to be 1,343 cubic centimeters.

Sample Composition No. 22 was prepared by mixing 0.35% of an acrylamide copolymer derivative (HALAD®-344) by weight of cement with a 15.8 ppg slurry of TXI Class H cement. The fluid loss was found to be 64 cubic centimeters.

Sample Composition No. 23 was prepared by mixing 0.35% of an acrylamide copolymer derivative (HALAD®-344) by weight of cement and 0.0157% of a hydrated polymer (CARBOTRON 20) by weight of cement with a 15.8 ppg slurry of TXI Class H cement. The fluid loss was found to be 60 cubic centimeters.

Sample Composition No. 24 was prepared by mixing 0.35% of an acrylamide copolymer derivative (HALAD®-344) by weight of cement, 0.0157% of a hydrated polymer (CARBOTRON 20) by weight of cement, and 0.204% of a dispersant (CFR-3) by weight of cement, with a 15.8 ppg slurry of TXI Class H cement. The fluid loss was found to be 44 cubic centimeters.

Sample Composition No. 25 was prepared by mixing a 15.8 ppg slurry of TXI Class H cement with 0.7% of a fluid loss additive comprising 47.5% of an acrylamide copolymer derivative (HALAD®-344) by weight, 47.5% Universal Cement Systems™ multi-purpose cement additive by weight, and 5% zeolite by weight. Accordingly, Sample Composition No. 25 contained 0.3325% HALAD®-344 by weight of cement, 0.3325% Universal Cement Systems™ multi-purpose cement additive by weight of cement, and 0.035% zeolite by weight of cement. The fluid loss was found to be 44 cubic centimeters.

Sample Composition No. 26 was prepared by mixing 0.35% of an acrylamide copolymer derivative (HALAD®-344) by weight of cement and 0.204% of a dispersant (CFR-3) by weight of cement, with a 15.8 ppg slurry of TXI Class H cement. The fluid loss was found to be 48 cubic centimeters.

A summary of the data from each of the samples is depicted in Table 5, below.

TABLE 5

FLUID	% Universal Cement Systems ™	% HALAD® -344	% Zeolite	% CARBOTRON 20	% CFR- 3	FLUID LOSS (cc)
Sample Composition No. 20	0	0	0	0	0	1,529
Sample Composition No. 21	0.35	0	0	0	0	1,343
Sample Composition No. 22	0	0.35	0	0	0	64
Sample Composition No. 23	0	0.35	0	0.0157	0	60
Sample Composition No. 24	0	0.35	0	0.0157	0.204	44
Sample Composition No. 25	0.3325	0.33250	0.035	0	0	44
Sample Composition No. 26	0	0.35	0	0	0.204	48

Inter alia, Example 8 demonstrates that the addition of, *inter alia*, a zeolite, a hydratable polymer, and a dispersant, to an acrylamide copolymer derivative provide improved fluid loss control.

Therefore, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those that are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.

What is claimed is:

1. A method of cementing in a subterranean formation comprising the steps of:
providing a cement composition comprising a hydraulic cement, water, and a fluid loss control additive, the fluid loss control additive comprising:
an acrylamide copolymer derivative; and
a hydratable polymer;
placing the cement composition into the subterranean formation; and
permitting the cement composition to set therein.
2. The method of claim 1 wherein the acrylamide copolymer derivative comprises a copolymer or copolymer salt of N,N-dimethylacrylamide and 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.
3. The method of claim 1 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member selected from the group consisting of lignin, lignite and their salts and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.
4. The method of claim 1 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member selected from the group consisting of derivatized cellulose, polyvinyl alcohol, polyethylene oxide, polypropylene oxide, and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.
5. The method of claim 1 wherein the acrylamide copolymer derivative comprises copolymers or copolymer salts comprising 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.
6. The method of claim 5 wherein the copolymers or copolymer salts comprise copolymers of hydrolyzed acrylamide and 2-acrylamido-2-methylpropane sulfonic acid derivatives.

7. The method of claim 1 wherein the hydratable polymer comprises carboxymethylcellulose, hydroxyethylcellulose, carboxymethylhydroxyethylcellulose, vinyl sulfonated polymers, hydratable graft polymers, and mixtures thereof.

8. The method of claim 1 wherein the fluid loss control additive further comprises a dispersant.

9. The method of claim 8 wherein the dispersant comprises a water-soluble polymer prepared by the caustic-catalyzed condensation of formaldehyde with acetone wherein the polymer contains sodium sulfate groups.

10. The method of claim 1 wherein the fluid loss control additive further comprises a zeolite.

11. The method of claim 1 wherein the fluid loss control additive further comprises a dispersant and a zeolite.

12. The method of claim 11 wherein the fluid loss control additive further comprises iron chloride, an organic acid, a deaggregation agent, silica, or mixtures thereof.

13. The method of claim 1 wherein the cement comprises Portland cements, pozzolanic cements, gypsum cements, high alumina content cements, silica cements, or high alkalinity cements.

14. The method of claim 1 wherein the water is present in the cement composition in an amount sufficient to form a pumpable slurry.

15. The method of claim 1 wherein the water is present in the cement composition in an amount in the range of from about 15% to about 200% by weight of cement.

16. The method of claim 1 wherein the cement composition has a density in the range of from about 5 pounds per gallon to about 30 pounds per gallon.

17. The method of claim 1 wherein the cement composition further comprises a weighting agent, a defoamer, a surfactant, mica, fiber, bentonite, microspheres, fumed silica, a salt, vitrified shale, fly ash, a dispersant, a retardant or an accelerant.

18. The method of claim 1 wherein the fluid loss control additive is present in the cement composition in an amount sufficient to provide a desired degree of fluid loss control.

19. The method of claim 1 wherein the fluid loss control additive is present in the cement composition in an amount in the range of from about 0.01% by weight of cement to about 5.0% by weight of cement.

20. The method of claim 12 wherein the iron chloride is present in the fluid loss control additive in an amount sufficient to allow the cement to be suitable for the subterranean temperature of the well being cemented.

21. The method of claim 12 wherein the iron chloride is present in the fluid loss control additive in an amount in the range of from about 5% to about 25% by weight of the fluid loss control additive.

22. The method of claim 12 wherein the iron chloride is anhydrous ferric chloride.

23. The method of claim 8 wherein the dispersant is present in the fluid loss control additive in an amount sufficient to prevent gelation of the cement composition.

24. The method of claim 8 wherein the dispersant is present in the fluid loss control additive in an amount in the range of from about 25% to about 50% by weight of the fluid loss control additive.

25. The method of claim 1 wherein the hydratable polymer is present in the fluid loss control additive in an amount in the range of from about 0.1% to about 15% by weight of the fluid loss control additive.

26. The method of claim 12 wherein the organic acid is present in the fluid loss control additive in an amount sufficient to provide a desired degree of viscosity control.

27. The method of claim 12 wherein the organic acid is present in the fluid loss control additive in an amount in the range of from about 0.01% to about 5% by weight of the fluid loss control additive.

28. The method of claim 12 wherein the silica is high surface area amorphous silica.

29. The method of claim 12 wherein the de-aggregation agent is present in the fluid loss control additive in an amount sufficient to enable the fluid loss control additive to flow freely as a powder.

30. The method of claim 29 wherein the de-aggregation agent is present in the fluid loss control additive in an amount in the range of from about 1% to about 15% by weight of the fluid loss control additive.

31. The method of claim 28 wherein the high surface area amorphous silica is present in the fluid loss control additive in an amount sufficient to provide a desired after-set compressive strength.

32. The method of claim 28 wherein the high surface area amorphous silica is present in the fluid loss control additive in an amount in the range of from about 0.1% to about 15% by weight of the fluid loss control additive.

33. The method of claim 1 wherein the acrylamide copolymer derivative is present in the fluid loss control additive in an amount in the range of from about 1% to about 99% by weight.

34. The method of claim 2 wherein the copolymer or copolymer salt has a N,N-dimethylacrylamide to 2-acrylamido-2-methylpropane sulfonic acid (or acid salts thereof) mole ratio of from about 1:4 to about 4:1.

35. The method of claim 2 wherein the copolymer or copolymer salt has a weight average molecular weight of between about 75,000 and about 300,000 daltons.

36. The method of claim 10 wherein the zeolite further comprises chabazite and amorphous silica.

37. The method of claim 10 wherein the zeolite is present in the fluid loss control additive in an amount in the range of from about 0.1% to about 15% by weight of the fluid loss control additive.

38. The method of claim 1 wherein the fluid loss control additive is present in the cement composition in an amount in the range of from about 0.25% to about 1.5% by weight of the cement; wherein the hydratable polymer is present in the fluid loss control additive in an amount in the range of from about 1.5% to about 4.5% by weight; wherein the acrylamide copolymer derivative is present in the fluid loss control additive in an amount in the range of from about 40% by weight to about 50% by weight; wherein the dispersing agent is present in the fluid loss control additive in an amount in the range of from about 40% to about 60% by weight; wherein the zeolite is present in the fluid loss control additive in an amount in the range of from about 1% by weight to about 10% by weight.

39. A method of cementing in a subterranean formation comprising the steps of:
providing a cement composition comprising a hydraulic cement, water, and a fluid loss control additive, the fluid loss control additive comprising:

an acrylamide copolymer derivative; and
a dispersant;

placing the cement composition into the subterranean formation; and
permitting the cement composition to set therein.

40. The method of claim 39 wherein the acrylamide copolymer derivative comprises a copolymer or copolymer salt of N,N-dimethylacrylamide and 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.

41. The method of claim 39 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member selected from the group consisting of lignin, lignite and their salts and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.

42. The method of claim 39 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member selected from the group consisting of derivatized cellulose, polyvinyl alcohol, polyethylene oxide, polypropylene oxide, and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.

43. The method of claim 39 wherein the acrylamide copolymer derivative comprises copolymers or copolymer salts comprising 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.

44. The method of claim 43 wherein the copolymers or copolymer salts comprise copolymers of hydrolyzed acrylamide and 2-acrylamido-2-methylpropane sulfonic acid derivatives.

45. The method of claim 39 wherein the fluid loss control additive further comprises a hydratable polymer and zeolite.

46. A method of reducing the fluid loss from a cement composition, comprising the step of adding to the cement composition a fluid loss control additive comprising:

an acrylamide copolymer derivative; and
a hydratable polymer.

47. The method of claim 46 wherein the acrylamide copolymer derivative comprises a copolymer or copolymer salt of N,N-dimethylacrylamide and 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.

48. The method of claim 46 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member selected from the group consisting of lignin, lignite and their salts and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.

49. The method of claim 46 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member selected from the group consisting of derivatized cellulose, polyvinyl alcohol, polyethylene oxide, polypropylene oxide, and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.

50. The method of claim 46 wherein the acrylamide copolymer derivative comprises copolymers or copolymer salts comprising 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.

51. The method of claim 50 wherein the copolymers or copolymer salts comprise copolymers of hydrolyzed acrylamide and 2-acrylamido-2-methylpropane sulfonic acid derivatives.

52. The method of claim 46 wherein the hydratable polymer comprises carboxymethylcellulose, hydroxyethylcellulose, carboxymethylhydroxyethylcellulose, vinyl sulfonated polymers, hydratable graft polymers, and mixtures thereof.

53. The method of claim 46 wherein the fluid loss control additive further comprises a dispersant.

54. The method of claim 53 wherein the dispersant comprises a water-soluble polymer prepared by the caustic-catalyzed condensation of formaldehyde with acetone wherein the polymer contains sodium sulfate groups.

55. The method of claim 46 wherein the fluid loss control additive further comprises a zeolite.

56. The method of claim 46 wherein the fluid loss control additive further comprises a dispersant and a zeolite.

57. The method of claim 56 wherein the fluid loss control additive further comprises iron chloride, an organic acid, a deaggregation agent, silica, or mixtures thereof.

58. The method of claim 46 wherein the cement composition comprises Portland cements, pozzolanic cements, gypsum cements, high alumina content cements, silica cements, or high alkalinity cements.

59. The method of claim 46 wherein the cement composition comprises water present in an amount sufficient to form a pumpable slurry.

60. The method of claim 59 wherein the water is present in the cement composition in an amount in the range of from about 15% by weight of cement to about 200% by weight of cement.

61. The method of claim 46 wherein the cement composition has a density in the range of from about 5 pounds per gallon to about 30 pounds per gallon.

62. The method of claim 46 wherein the cement composition further comprises a weighting agent, a defoamer, a surfactant, mica, fiber, bentonite, microspheres, fumed silica, a salt, vitrified shale, fly ash, a dispersant, a retardant or an accelerant.

63. The method of claim 46 wherein the fluid loss control additive is present in the cement composition in an amount sufficient to provide a desired degree of fluid loss control.

64. The method of claim 46 wherein the fluid loss control additive is present in the cement composition in an amount in the range of from about 0.01% by weight of cement to about 5.0% by weight of cement.

65. The method of claim 57 wherein the iron chloride is present in the fluid loss control additive in an amount sufficient to allow the cement to be suitable for the subterranean temperature of the well being cemented.

66. The method of claim 57 wherein the iron chloride is present in the fluid loss control additive in an amount in the range of from about 5% to about 25% by weight of the fluid loss control additive.

67. The method of claim 57 wherein the iron chloride is anhydrous ferric chloride.

68. The method of claim 53 wherein the dispersant is present in the fluid loss control additive in an amount sufficient to prevent gelation of the cement composition.

69. The method of claim 53 wherein the dispersant is present in the fluid loss control additive in an amount in the range of from about 25% to about 50% by weight of the fluid loss control additive.

70. The method of claim 46 wherein the hydratable polymer is present in the fluid loss control additive in an amount in the range of from about 0.1% to about 15% by weight of the fluid loss control additive.

71. The method of claim 57 wherein the organic acid is present in the fluid loss control additive in an amount sufficient to provide a desired degree of viscosity control.

72. The method of claim 57 wherein the organic acid is present in the fluid loss control additive in an amount in the range of from about 0.01% to about 5% by weight of the fluid loss control additive.

73. The method of claim 57 wherein the silica is high surface area amorphous silica.

74. The method of claim 57 wherein the de-aggregation agent is present in the fluid loss control additive in an amount sufficient to enable the fluid loss control additive to flow freely as a powder.

75. The method of claim 57 wherein the de-aggregation agent is present in the fluid loss control additive in an amount in the range of from about 1% to about 15% by weight of the fluid loss control additive.

76. The method of claim 73 wherein the high surface area amorphous silica is present in the fluid loss control additive in an amount sufficient to provide a desired after-set compressive strength.

77. The method of claim 73 wherein the high surface area amorphous silica is present in the fluid loss control additive in an amount in the range of from about 0.1% to about 15% by weight of the fluid loss control additive.

78. The method of claim 46 wherein the acrylamide copolymer derivative is present in the fluid loss control additive in an amount in the range of from about 1% to about 99% by weight.

79. The method of claim 47 wherein the copolymer or copolymer salt has a N,N-dimethylacrylamide to 2-acrylamido-2-methylpropane sulfonic acid (or acid salts thereof) mole ratio of from about 1:4 to about 4:1.

80. The method of claim 47 wherein the copolymer or copolymer salt has a weight average molecular weight of between about 75,000 and about 300,000 daltons.

81. The method of claim 55 wherein the zeolite further comprises chabazite and amorphous silica.

82. The method of claim 55 wherein the zeolite is present in the fluid loss control additive in an amount in the range of from about 0.1% to about 15% by weight.

83. The method of claim 46 wherein the fluid loss control additive is present in the cement composition in an amount in the range of from about 0.25% to about 1.5% by weight of the cement; wherein the hydratable polymer is present in the fluid loss control additive in an amount in the range of from about 1.5% to about 4.5% by weight; wherein the acrylamide copolymer derivative is present in the fluid loss control additive in an amount in the range of from about 40% by weight to about 50% by weight; wherein the dispersing agent is present in the fluid loss control additive in an amount in the range of from about 40% to about 60% by weight; wherein the zeolite is present in the fluid loss control additive in an amount in the range of from about 1% by weight to about 10% by weight.

84. A method of reducing the fluid loss from a cement composition, comprising the step of adding to the cement composition a fluid loss control additive comprising:

an acrylamide copolymer derivative; and
a dispersant.

85. The method of claim 84 wherein the acrylamide copolymer derivative comprises a copolymer or copolymer salt of N,N-dimethylacrylamide and 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.

86. The method of claim 84 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member selected from the group consisting of lignin, lignite and their salts and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.

87. The method of claim 84 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member selected from the group consisting of derivatized cellulose, polyvinyl alcohol, polyethylene oxide, polypropylene oxide, and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.

88. The method of claim 84 wherein the acrylamide copolymer derivative comprises copolymers or copolymer salts comprising 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.

89. The method of claim 88 wherein the copolymers or copolymer salts comprise copolymers of hydrolyzed acrylamide and 2-acrylamido-2-methylpropane sulfonic acid derivatives.

90. The method of claim 84 wherein the fluid loss control additive further comprises a hydratable polymer and zeolite.

91. A cement composition comprising a hydraulic cement, water, and a fluid loss control additive, the fluid loss control additive comprising:

an acrylamide copolymer derivative; and
a hydratable polymer.

92. The cement composition of claim 91 wherein the acrylamide copolymer derivative comprises a copolymer or copolymer salt of N,N-dimethylacrylamide and 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.

93. The cement composition of claim 91 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member selected from the group consisting of lignin, lignite and their salts and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.

94. The cement composition of claim 91 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member

selected from the group consisting of derivatized cellulose, polyvinyl alcohol, polyethylene oxide, polypropylene oxide, and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.

95. The cement composition of claim 91 wherein the acrylamide copolymer derivative comprises copolymers or copolymer salts comprising 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.

96. The cement composition of claim 95 wherein the copolymers or copolymer salts comprise copolymers of hydrolyzed acrylamide and 2-acrylamido-2-methylpropane sulfonic acid derivatives.

97. The cement composition of claim 91 wherein the hydratable polymer comprises carboxymethylcellulose, hydroxyethylcellulose, carboxymethylhydroxyethylcellulose, vinyl sulfonated polymers, hydratable graft polymers, and mixtures thereof.

98. The cement composition of claim 91 wherein the fluid loss control additive further comprises a dispersant.

99. The cement composition of claim 98 wherein the dispersant comprises a water-soluble polymer prepared by the caustic-catalyzed condensation of formaldehyde with acetone wherein the polymer contains sodium sulfate groups.

100. The cement composition of claim 91 wherein the fluid loss control additive further comprises a zeolite.

101. The cement composition of claim 91 wherein the fluid loss control additive further comprises a dispersant and a zeolite.

102. The cement composition of claim 101 wherein the fluid loss control additive further comprises iron chloride, an organic acid, a deaggregation agent, silica, or mixtures thereof.

103. The cement composition of claim 91 wherein the hydraulic cement comprises Portland cements, pozzolanic cements, gypsum cements, high alumina content cements, silica cements, or high alkalinity cements.

104. The cement composition of claim 91 wherein the water is present in the cement composition in an amount sufficient to form a pumpable slurry.

105. The cement composition of claim 91 wherein the water is present in the cement composition in an amount in the range of from about 15% by weight of cement to about 200% by weight of cement.

106. The cement composition of claim 91 wherein the cement composition has a density in the range of from about 5 pounds per gallon to about 30 pounds per gallon.

107. The cement composition of claim 91 wherein the cement composition further comprises a weighting agent, a defoamer, a surfactant, mica, fiber, bentonite, microspheres, fumed silica, a salt, vitrified shale, fly ash, a dispersant, a retardant or an accelerator.

108. The cement composition of claim 91 wherein the fluid loss control additive is present in the cement composition in an amount sufficient to provide a desired degree of fluid loss control.

109. The cement composition of claim 91 wherein the fluid loss control additive is present in the cement composition in an amount in the range of from about 0.01% by weight of cement to about 5.0% by weight of cement.

110. The cement composition of claim 102 wherein the iron chloride is present in the fluid loss control additive in an amount sufficient to allow the cement to be suitable for the subterranean temperature of the well being cemented.

111. The cement composition of claim 102 wherein the iron chloride is present in the fluid loss control additive in an amount in the range of from about 5% to about 25% by weight of the fluid loss control additive.

112. The cement composition of claim 102 wherein the iron chloride is anhydrous ferric chloride.

113. The cement composition of claim 98 wherein the dispersant is present in the fluid loss control additive in an amount sufficient to prevent gelation of the cement composition.

114. The cement composition of claim 98 wherein the dispersant is present in the fluid loss control additive in an amount in the range of from about 25% to about 50% by weight of the fluid loss control additive.

115. The cement composition of claim 91 wherein the hydratable polymer is present in the fluid loss control additive in an amount in the range of from about 0.1% to about 15% by weight of the fluid loss control additive.

116. The cement composition of claim 102 wherein the organic acid is present in the fluid loss control additive in an amount sufficient to provide a desired degree of viscosity control.

117. The cement composition of claim 102 wherein the organic acid is present in the fluid loss control additive in an amount in the range of from about 0.01% to about 5% by weight of the fluid loss control additive.

118. The cement composition of claim 102 wherein the silica is high surface area amorphous silica.

119. The cement composition of claim 102 wherein the de-aggregation agent is present in the fluid loss control additive in an amount sufficient to enable the fluid loss control additive to flow freely as a powder.

120. The cement composition of claim 102 wherein the de-aggregation agent is present in the fluid loss control additive in an amount in the range of from about 1% to about 15% by weight of the fluid loss control additive.

121. The cement composition of claim 118 wherein the high surface area amorphous silica is present in the fluid loss control additive in an amount sufficient to provide a desired after-set compressive strength.

122. The cement composition of claim 118 wherein the high surface area amorphous silica is present in the fluid loss control additive in an amount in the range of from about 0.1% to about 15% by weight of the fluid loss control additive.

123. The cement composition of claim 91 wherein the acrylamide copolymer derivative is present in the fluid loss control additive in an amount in the range of from about 1% to about 99% by weight.

124. The cement composition of claim 92 wherein the copolymer or copolymer salt has a N,N-dimethylacrylamide to 2-acrylamido-2-methylpropane sulfonic acid (or acid salts thereof) mole ratio of from about 1:4 to about 4:1.

125. The cement composition of claim 92 wherein the copolymer or copolymer salt has a weight average molecular weight of between about 75,000 and about 300,000 daltons.

126. The cement composition of claim 100 wherein the zeolite further comprises chabazite and amorphous silica.

127. The cement composition of claim 100 wherein the zeolite is present in the fluid loss control additive in an amount in the range of from about 0.1% to about 15% by weight of the fluid loss control additive.

128. The cement composition of claim 91 wherein the fluid loss control additive is present in the cement composition in an amount in the range of from about 0.25% to about 1.5% by weight of the cement; wherein the hydratable polymer is present in the fluid loss control additive in an amount in the range of from about 1.5% to about 4.5% by weight; wherein the acrylamide copolymer derivative is present in the fluid loss control additive in an amount in the range of from about 40% by weight to about 50% by weight; wherein the dispersing agent is present in the fluid loss control additive in an amount in the range of from about in the range of from about 40% to about 60% by weight; wherein the zeolite is present in the fluid loss control additive in an amount in the range of from about 1% by weight to about 10% by weight.

129. A cement composition comprising a hydraulic cement, water, and a fluid loss control additive, the fluid loss control additive comprising:

an acrylamide copolymer derivative; and
a dispersant.

130. The cement composition of claim 129 wherein the acrylamide copolymer derivative comprises a copolymer or copolymer salt of N,N-dimethylacrylamide and 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.

131. The cement composition of claim 129 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member selected from the group consisting of lignin, lignite and their salts and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.

132. The cement composition of claim 129 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member

selected from the group consisting of derivatized cellulose, polyvinyl alcohol, polyethylene oxide, polypropylene oxide, and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.

133. The cement composition of claim 129 wherein the acrylamide copolymer derivative comprises copolymers or copolymer salts comprising 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.

134. The cement composition of claim 133 wherein the copolymers or copolymer salts comprise copolymers of hydrolyzed acrylamide and 2-acrylamido-2-methylpropane sulfonic acid derivatives.

135. The cement composition of claim 129 wherein the fluid loss control additive further comprises a hydratable polymer and zeolite.

136. A fluid loss control additive comprising:
an acrylamide copolymer derivative; and
a hydratable polymer.

137. The fluid loss control additive of claim 136 wherein the acrylamide copolymer derivative comprises a copolymer or copolymer salt of N,N-dimethylacrylamide and 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.

138. The fluid loss control additive of claim 136 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member selected from the group consisting of lignin, lignite and their salts and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.

139. The fluid loss control additive of claim 136 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member selected from the group consisting of derivatized cellulose, polyvinyl alcohol, polyethylene oxide, polypropylene oxide, and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid,

acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.

140. The fluid loss control additive of claim 136 wherein the acrylamide copolymer derivative comprises copolymers or copolymer salts comprising 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.

141. The fluid loss control additive of claim 140 wherein the copolymers or copolymer salts comprise copolymers of hydrolyzed acrylamide and 2-acrylamido-2-methylpropane sulfonic acid derivatives.

142. The fluid loss control additive of claim 136 wherein the hydratable polymer comprises carboxymethylcellulose, hydroxyethylcellulose, carboxymethylhydroxyethylcellulose, vinyl sulfonated polymers, hydratable graft polymers, and mixtures thereof.

143. The fluid loss control additive of claim 136 further comprising a dispersant.

144. The fluid loss control additive of claim 143 wherein the dispersant comprises a water-soluble polymer prepared by the caustic-catalyzed condensation of formaldehyde with acetone wherein the polymer contains sodium sulfate groups.

145. The fluid loss control additive of claim 136 further comprising a zeolite.

146. The fluid loss control additive of claim 136 further comprising a dispersant and a zeolite.

147. The fluid loss control additive of claim 146 further comprising iron chloride, an organic acid, a deaggregation agent, silica, or mixtures thereof.

148. The fluid loss control additive of claim 147 wherein the iron chloride is present in an amount sufficient to allow a cement composition to be suitable for the subterranean temperature of the well being cemented.

149. The fluid loss control additive of claim 147 wherein the iron chloride is present in an amount in the range of from about 5% to about 25% by weight of the fluid loss control additive.

150. The fluid loss control additive of claim 147 wherein the iron chloride is anhydrous ferric chloride.

151. The fluid loss control additive of claim 143 wherein the dispersant is present in an amount sufficient to prevent gelation of a cement composition.

152. The fluid loss control additive of claim 143 wherein the dispersant is present in an amount in the range of from about 25% to about 50% by weight of the fluid loss control additive.

153. The fluid loss control additive of claim 136 wherein the hydratable polymer is present in an amount in the range of from about 0.1% to about 15% by weight of the fluid loss control additive.

154. The fluid loss control additive of claim 147 wherein the organic acid is present in an amount sufficient to provide a desired degree of viscosity control.

155. The fluid loss control additive of claim 147 wherein the organic acid is present in an amount in the range of from about 0.01% to about 5% by weight of the fluid loss control additive.

156. The fluid loss control additive of claim 147 wherein the silica is high surface area amorphous silica.

157. The fluid loss control additive of claim 147 wherein the de-aggregation agent is present in an amount sufficient to enable the fluid loss control additive to flow freely as a powder.

158. The fluid loss control additive of claim 147 wherein the de-aggregation agent is present in an amount in the range of from about 1% to about 15% by weight of the fluid loss control additive.

159. The fluid loss control additive of claim 156 wherein the high surface area amorphous silica is present in an amount sufficient to provide a desired after-set compressive strength.

160. The fluid loss control additive of claim 156 wherein the high surface area amorphous silica is present in an amount in the range of from about 0.1% to about 15% by weight of the fluid loss control additive.

161. The fluid loss control additive of claim 136 wherein the acrylamide copolymer derivative is present in an amount in the range of from about 1% to about 99% by weight.

162. The fluid loss control additive of claim 137 wherein the copolymer or copolymer salt has a N,N-dimethylacrylamide to 2-acrylamido-2-methylpropane sulfonic acid (or acid salts thereof) mole ratio of from about 1:4 to about 4:1.

163. The fluid loss control additive of claim 137 wherein the copolymer or copolymer salt has a weight average molecular weight of between about 75,000 and about 300,000 daltons.

164. The fluid loss control additive of claim 145 wherein the zeolite further comprises chabazite and amorphous silica.

165. The fluid loss control additive of claim 145 wherein the zeolite is present in an amount in the range of from about 0.1% to about 15% by weight.

166. The fluid loss control additive of claim 136 wherein the fluid loss control additive is present in the cement composition in an amount in the range of from about 0.25% to about 1.5% by weight of the cement; wherein the hydratable polymer is present in the fluid loss control additive in an amount in the range of from about 1.5% to about 4.5% by weight; wherein the acrylamide copolymer derivative is present in the fluid loss control additive in an amount in the range of from about 40% by weight to about 50% by weight; wherein the dispersing agent is present in the fluid loss control additive in an amount in the range of from about in the range of from about 40% to about 60% by weight; wherein the zeolite is present in the fluid loss control additive in an amount in the range of from about 1% by weight to about 10% by weight.

167. A fluid loss control additive comprising:
an acrylamide copolymer derivative; and
a dispersant.

168. The fluid loss control additive of claim 167 wherein the acrylamide copolymer derivative comprises a copolymer or copolymer salt of N,N-dimethylacrylamide and 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.

169. The fluid loss control additive of claim 167 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member selected from the group consisting of lignin, lignite and their salts and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.

170. The fluid loss control additive of claim 167 wherein the acrylamide copolymer derivative comprises a graft polymer comprising a backbone comprising at least one member

selected from the group consisting of derivatized cellulose, polyvinyl alcohol, polyethylene oxide, polypropylene oxide, and a grafted pendant group comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate wherein the alkyl radical comprises at least one member selected from the group consisting of methyl, ethyl and propyl radicals.

171. The fluid loss control additive of claim 167 wherein the acrylamide copolymer derivative comprises copolymers or copolymer salts comprising 2-acrylamido-2-methylpropane sulfonic acid or acid salts thereof.

172. The fluid loss control additive of claim 171 wherein the copolymers or copolymer salts comprise copolymers of hydrolyzed acrylamide and 2-acrylamido-2-methylpropane sulfonic acid derivatives.

173. The fluid loss control additive of claim 167 further comprising a hydratable polymer and a zeolite.

174. The fluid loss control additive of claim 167 wherein the dispersant comprises a water-soluble polymer prepared by the caustic-catalyzed condensation of formaldehyde with acetone wherein the polymer contains sodium sulfate groups.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/001648

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C04B28/02 C04B24/26 C04B24/38 C04B26/28 C04B22/12
E21B33/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C04B E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- "Z" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 September 2004	01/10/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax (+31-70) 340-3016	Authorized officer Burtran, M-M

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/001648

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 676 317 A (CHILDS JERRY D ET AL) 30 June 1987 (1987-06-30)	1-3, 5-8, 13-19, 23-35, 39-41, 43, 44, 46-48, 50-53, 58-64, 68-80, 84-86, 88, 89, 91-93, 95-98, 103-109, 113-125, 129-131, 133, 134, 136-138, 140-143, 151-163, 167-169, 171, 172 9, 20-22, 54, 65-67, 99, 110-112, 144, 148-150, 174 10-12, 36-38, 45, 55-57, 81-83, 90, 100-102, 126-128, 135, 147, 148, 164-166, 173
Y		
Y		
	abstract column 2, line 51 - column 3, line 34 examples 1-4 tables 1-4 claims 1-19	----- -/-

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/001648

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 703 801 A (CHILDS JERRY D ET AL) 3 November 1987 (1987-11-03)	1,2,4-8, 13-19, 23-35, 39,40, 42-44, 46,47, 49-53, 58-64, 68-80, 84,85, 87-89, 91,92, 94-98, 103-109, 113-125, 129,130, 132-134, 136,137, 139-143, 151-163, 167,168, 170-172
X	abstract column 2, line 53 - column 3, line 36 examples 1-4 tables 1-4 claims 1-12	
Y	US 5 968 255 A (GRAY DENNIS W ET AL) 19 October 1999 (1999-10-19)	9,20-22, 54, 65-67, 99, 110-112, 144, 148-150, 174
Y	column 6, line 20 - line 42 claims 1,14,16,26	
Y	WO 00/41981 A (WAIN CHRISTOPHER PAUL ; HALLIBURTON ENERGY SERV INC (US)) 20 July 2000 (2000-07-20)	10-12, 36-38, 45, 55-57, 81-83, 90, 100-102, 126-128, 135,147, 148, 164-166, 173
	page 4, line 27 - page 5, line 19 claims 1,2,10,12,21,22,32,33,45,46,55,56,59	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2004/001648

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.:

14, 18, 20, 23, 26, 29, 31, 59, 63, 65, 68, 71, 74, 76, 104, 108, 110, 113, 116, 119, 121, 148, 151, 154, 157, 159 (all partially)

Present claims

14, 18, 20, 23, 26, 29, 31, 59, 63, 65, 68, 71, 74, 76, 104, 108, 110, 113, 116, 119, 121, 148, 151, 154, 157 and 159 relate to methods and products defined by reference to several desirable characteristics, namely "in an amount sufficient to form a pumpable slurry" (claims 14, 59 and 104), "in an amount sufficient to provide a desired degree of fluid loss control" (claims 18, 63 and 108), "in an amount sufficient to allow the cement to be suitable for the subterranean temperature" (claims 20, 65, 110 and 148), "in an amount sufficient to prevent gelation" (claims 23, 68, 113 and 151), "in an amount sufficient to provide a desired degree of viscosity control" (claims 26, 71, 116 and 154), "in an amount sufficient to enable the fluid loss control additive to flow freely as a powder" (claims 29, 74, 119 and 157) and "in an amount sufficient to provide a desired after-set compressive strength" (claims 31, 76, 121 and 159). The claims cover an extremely large number of methods and products having these characteristics, whereas the application provides support within the meaning of Article 6 PCT and disclosure within the meaning of Article 5 PCT for only a very limited number of such methods and products. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the methods and products of said claims respectively by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely those parts relating to the methods and products wherein:

1. the water content of the cement composition is from 15% to 200% by weight of cement (claims 15, 60 and 105);
2. the amount of fluid loss control additive in the cement composition is from 0.01% to 5.0% by weight of cement (claims 19, 64 and 109);
3. the amount of iron chloride in the fluid loss control additive is from 5% to 25% by weight of additive (claims 21, 66, 111 and 149);
4. the amount of dispersant in the fluid loss control additive is from 25% to 50% by weight of additive (claims 24, 69, 114 and 152);
5. the amount of organic acid in the fluid loss control additive is from 0.01% to 5% by weight of additive (claims 27, 71, 117 and 155);
6. the amount of de-aggregation agent in the fluid loss control additive is from 1% to 15% by weight of additive (claims 30, 75, 120 and 158);
7. the amount of amorphous silica in the fluid loss control additive is from 0.1% to 15% by weight of additive (claims 32, 77, 122 and 160);

and a fair generalization thereof.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB2004/001648

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